(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 984 038 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.03.2000 Bulletin 2000/10

(51) Int. Cl.^{7}: **C08L 53/02**, C08F 297/04

(21) Application number: 99202818.3

(22) Date of filing: **31.08.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **04.09.1998 IT MI981960**

(71) Applicant: **Enichem S.p.A.**
20097 S. Donato Milanese (Milano) (IT)

(72) Inventors:
- **Cavallo, Claudio**
  47100 Forli (IT)
- **Custro, Sergio**
  48100 Ravenna (IT)
- **Viola, Gian Tommaso**
  48015 Cervia, Ravenna (IT)

(74) Representative:
De Gregori, Antonella et al
Ing. Barzano & Zanardo Milano S.p.A.
Via Borgonuovo 10
20121 Milano (IT)

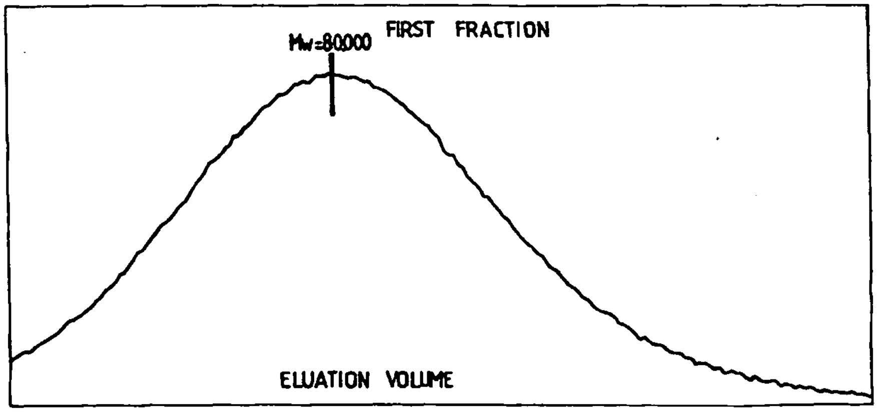
(54) Hydrogenated block copolymers having a partially branched structure

(57) Composition of vinylarene/hydrogenated diene block copolymers, the latter being selected from ethylene-butene and ethylene-propylene, characterized in that it comprises:

a) copolymers having linear structures from 30% to 60% by weight, preferably from 35% to 50%;
b) copolymers having branched structures from 70% to 40% by weight, preferably from 65% to 50%;

the sum of components (a) and (b) being equal to 100; the weight average molecular weight of the above composition ranging from 30,000 to 400,000, preferably from 50,000 to 200,000.

Fig.1

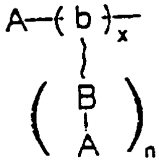


Description

[0001] The present invention relates to a composition of hydrogenated block copolymers having an optimum balance between mechanical properties and rheological properties.
[0002] The present invention also relates to the process for the preparation of the above copolymers.
[0003] Vinyl-arene/hydrogenated diene block copolymers are characterized by a very high viscosity compared with analogous non-hydrogenated products. From the point of view of application, this characteristic represents a great limit; it is therefore often necessary to resort to formulations in which the copolymer is diluted with fillers or other polymers having a lower viscosity. This often causes a reduction in the mechanical properties of the mixture and can therefore not always be put into use.
[0004] A partial first solution of the above problem is the use of linear multi-block structures (see for example US-A-5,164,455) and star structures of the $(AB)_x$type wherein x is a number from 3 to 6.
[0005] These copolymers, both with a linear multi-block and star structure, also have the disadvantage of not being entirely suitable for balancing the rheological properties with the mechanical properties.
[0006] A composition of block copolymers has now been found, which overcomes the drawbacks described above.
[0007] In accordance with this, the present invention relates to a composition of vinylarene/hydrogenated diene block copolymers, the latter selected from ethylene-butene and ethylene-propylene, characterized in that it comprises:

(a) from 30% to 60% by weight, preferably from 35% to 50%, of copolymers having linear structures;
(b) from 70% to 40% by weight, preferably from 65% to 50%, of copolymers having branched structures;

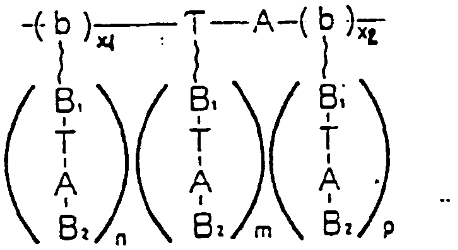
the sum of components (a) and (b) being equal to 100;
the weight average molecular weight of the above composition ranging from 30,000 to 400,000, preferably from 50,000 to 200,000.
[0008] The weight content of vinylarene in the polymeric composition of the present invention ranges from 2 to 75%, preferably from 5 to 40%, with a weight percentage of block vinylarene ranging from 50% to 100% of the total vinylarene. The vinylarene content can be regulated as desired depending on the end use of the polymeric composition of the present invention.
[0009] In the preferred embodiment the vinylarene is styrene.
[0010] The term "linear structures" refers to structures of the type $(A\text{-}B)_a$ and $(B\text{-}TA\text{-}B)_a$ wherein A, B, T will be defined further on and "a" indicates the number of blocks and is an integer ranging from 1 to 3.
[0011] The term "branched structures" refers to structures selected from those having general formula (I)



$$A-\underset{\underset{\begin{pmatrix}B\\ |\\ A\end{pmatrix}_n}{|}}{(b)}_x- \qquad (I)$$

wherein:

1) A is the polyvinylarene block;
2) b is the monomeric unit of hydrogenated diene, selected from ethylene-butene and ethylene-propylene;
3) x is the number of monomeric units which form the ethylene-butene or ethylene-propylene block;
4) B is the hydrogenated polydiene block-$(b)_x$-;
5) n is the number of branches of the copolymer and is an integer ranging from 1 to 5;
6) B-A is the block copolymer grafted onto the hydrogenated polydiene fraction -(-b-)$_x$-;
or from those having general formula (II):



(II)

wherein:

7) A, B and b have the meaning defined above;
8) x_1 and x_2 are the number of hydrogenated diene monomeric units which form the two ethylene/butene or ethylene/propylene blocks;
9) T is the statistic terpolymer consisting of vinylarene/ethylene-butene or vinylarene/ethylene-propylene, the content of T being from 0 to 30% by weight of the compound having general formula (II);
10) $-B_1-T-A-B_2$ is the block copolymer grafted onto $-(-b-)_{x1}-T-A-(-b-)_{x2}-$;
11) $(m+n+p)$ is the number of branches of the copolymer $-B_1-T-A-B_2$ grafted and ranges from 1 to 5.

[0012] The composition of the present invention can be obtained by means of a particular process which comprises the use of a hydrocarbon monobromo-derivative, particularly a monobromo alkyl derivative, with the formation of a "parent" polymer subsequently subjected to selective hydrogenation.

[0013] The composition of the present invention has an excellent balance of rheological properties and technological properties.

[0014] The present invention also relates to a process for the preparation of the polymeric composition defined above which comprises the following steps:

a) reaction of a vinylarene, as such or mixed with a conjugated diene, with an organo-derivative of Lithium having the general formula R-Li wherein R is a monofunctional hydrocarbon radical selected from aliphatic and cycloaliphatic radicals with from 2 to 20 carbon atoms;
b) reaction of the mixture coming from step (a) with a conjugated diene;
c) reaction of the mixture coming from step (b) with a bromo-derivative having the general formula R'-Br in an essentially stoichiometric quantity with respect to the Lithium, wherein R' is a C_1-C_{10} monofunctional hydrocarbon radical selected from alkyl, cycloalkyl and aryl radicals, R' is preferably a C_1-C_3 alkyl radical, even more preferably R' is ethyl; thus obtaining a composition of non-hydrogenated block copolymers;
d) hydrogenation of the polydiene section of the composition of non-hydrogenated block copolymers obtained in step (c) to give the composition of hydrogenated block copolymers of the present invention.

[0015] In the process described above, the bromo-derivative having general formula R'-Br acts as both branching agent and quenching agent and consequently an additional quenching step with reagents such as water and alcohols is not required.

[0016] Step (a) of the process consists in reacting the vinylarene (optionally mixed with the diene), preferably styrene, and the organo-alkyl derivative of lithium in an inert solvent with the formation of a living polymer having a simplified A-Li structure. Other vinyl arenes which can be used for the formation of the non-elastomeric thermoplastic block A, are alpha methyl styrene, terbutylstyrene and other styrenes alkylated in the ring and relative mixtures.

[0017] The inert solvent which can be used in step (a) can be an aromatic or naphthene hydrocarbon, for example benzene or cyclohexane, optionally modified by the presence of alkanes and alkenes, for example pentenes or pentanes. Examples of suitable solvents are toluene, benzene, xylene, cyclohexane, optionally mixed with n-pentane, n-hexane, iso-octane.

[0018] Examples of the organo-derivative of Lithium having formula R-Li are ethyl Lithium, n-propyl Lithium, iso-propyl Lithium, n-butyl Lithium, sec-butyl Lithium, ter-butyl Lithium, ter-octyl Lithium, decyl Lithium. The organo-derivative of Lithium is preferably selected from n-butyl Lithium and sec-butyl Lithium. The concentration of the Lithium alkyl initiator can be modified to control the molecular weight. The concentration of the above initiator generally ranges from 0.25 to 50 mmoles per 100 grams of monomer, even if there are no limits for using higher quantities.

[0019] The temperature during step (a) of the process of the present invention generally ranges from 10°C to 80°C, preferably from 30°C to 60°C, sufficient however to keep the monomers in liquid phase.

[0020] As soon as the whole vinylarene monomer, optionally mixed with the diene, has almost disappeared (and the living polymer has an A-Li structure), the conjugated diene having from 4 to 5 carbon atoms, preferably selected from isoprene and butadiene, even more preferably butadiene, is added (step b) to the solution obtained in step (a).

[0021] Once the diene-type monomer has been almost totally used up (consequently at the end of step (b)), the resulting polymer may have a block structure of the A-B-Li or B_1TA-B_2-Li type.

[0022] At the end of step (b), the polymeric solution is treated with the branching agent R'-Br at a temperature ranging from 40°C to 120°C, preferably from 70°C to 100°C. Examples of compounds having formula R'-Br which can be used in the present invention are monobromomethane, monobromoethane and upper homologous products, monobromocyclohexane, monobromobenzene and its alkyl derivatives. In the preferred embodiment, the compound having general formula R'-Br is monobromoethane. Step (c) is usually completed in a period of 5 to 30 minutes.

[0023] The polymer is then recovered and subjected to the hydrogenation process in which the polydiene part is selectively hydrogenated.

[0024] The hydrogenation process (step d) can be carried out using any of the processes known in the art for the hydrogenation of olefinic unsaturations in the presence of suitable catalysts. Among these, catalytic systems based on nickel carboxylates and aluminum alkyls, described in US-A-3,431,323, or systems based on metallocene compounds of titanium and magnesium alkyls described in patent application MI97A 002477, can be mentioned.

[0025] The above hydrogenated compositions can be widely used in many fields of application, for example in the formulation of adhesives and seals, in the modification of plastic materials and mixtures of plastic materials.

[0026] A first application consists in the preparation of adhesive formulations. Block copolymers do not normally have sufficient adhesive properties to enable them to be used alone. It is therefore necessary to add tacking resins compatible with the elastomeric block of the hydrogenated conjugated diene. The quantity of tacking resin contained in the formulation of the present invention ranges from 50 to 200 parts per 100 parts of rubber (phr), preferably from 50 to 150 phr. The adhesive formulations of the present invention may optionally also contain fluidizing substances; among these liquid polyterpene resins can be mentioned. Stabilizers and oxygen inhibitors are usually added to protect the polymers against degradation during the preparation and use of the adhesive composition. Examples of antioxidants which are commercially available are Ionox® 220, i.e. 3,4,6-tris(3,5-di-t-butyl-p-hydroxybenzyl)-1,3,5-trime-thylbenzene, Irganox® 1010 (a terbutyl hydroxyphenyl propionate) and Irganox® 565 (or a thiotriazine derivative).

[0027] The "hot-melt" adhesive composition generally contains one or more antioxidants in a quantity ranging from about 0.01 to about 2.0% by weight.

[0028] The adhesive compositions of the present invention can be prepared by mixing in a solvent (for example toluene) the block copolymers, the tacking resin and fluidizing substances such as for example liquid resin, and stripping the solvent; alternatively the above compositions can be prepared by the simple mixing of the components at a high temperature, for example at about 150°C (hot melt).

[0029] A preferred use of the polymeric compositions of the present invention, again in the field of adhesives, is in the preparation of adhesive tapes sensitive to pressure (PSA i.e. "pressure sensitive adhesives"), according to methods described in literature, for example in accordance with what is disclosed in US-A-3,676,202, or in the preparation of lables.

[0030] A second application consists in the modification of engineering polymers, particularly polyesters, polyamides and polycarbonates, particularly polycarbonate. Polycarbonate is, in fact, particularly fragile at low temperatures (<0°C) and cannot therefore be used as such in applications which comprise low operating temperatures. The addition to the polycarbonate of the polymeric composition of the present invention considerably increases the resistance to low temperatures of the end-articles based on polycarbonate, without jeopardizing the other properties. A further object of the present invention relates to a polymeric composition comprising engineering polymers, selected from polyesters, polyamides and polycarbonates, preferably polycarbonate, and the mixture of block copolymers of the present invention.

[0031] Another application of the polymeric composition of the present invention consists in rendering plastic materials compatible (for example polyethylene and polystyrene), which are otherwise incompatible, enabling the preparation of polymeric alloys having a combination of excellent properties. In accordance with this, the present invention also relates to a polymeric composition comprising polyethylene, polystyrene and the mixture of block copolymers of the present invention.

[0032] The following examples provide a better understanding of the present invention.

EXAMPLE 1

[0033] 8400 grams of cyclohexane, 23 ml of a 2M solution of di-tetrahydrofuran-propane in cyclohexane and 240 grams of styrene are charged into a 25 litre autoclave. The system is thermostat-regulated at 50°C and 20.6 ml of a 1.5 M solution in n-hexane of sec-butyl-lithium are then added.

[0034] After 30 minutes 960 g of butadiene are added to the polymeric solution thus obtained and the mixture is then left to react for 15 minutes. 12.5 ml of a 1M solution in cyclohexane of monobromoethane are then added, at a temperature of 95°C, and the mixture is left to react for 15 minutes. The polymer thus obtained has a 1,2 chain percentage in the polybutadiene section equal to 60%.

[0035] 4800 grams of the polymeric solution thus obtained are then transferred in an inert atmosphere (argon) to a 16 litre reactor and 0.310 g of bis cyclopentadienyltitanium di-chloride and 0.904 g of dibutyl-magnesium suitably premixed in cyclohexane, are then added. The polymeric solution is then brought into an H_2 atmosphere (24 bars) and maintained at a temperature of 100°C for 60 minutes.

[0036] The polymeric solution is subsequently discharged and antioxidant (Irganox® 1010, 0.1 phr with respect to the dry product) is added. The solvent is removed by distillation in a vapour stream and the polymer is dried on a fluid bed.

[0037] The polymer thus obtained has an average molecular weight (Mw) of 80,000 and consists of:

(a) a linear fraction (60%) having a molecular weight of 40,000;
(b) a branched fraction (40% by weight) having a molecular weight of 80,000 to 360,000.

[0038] The content of polystyrene with respect to the polymer, measured by means of Fourier transform infra-red spectrometry (FTIR), proved to be 20%. The hydrogenation degree of the polybutadiene section, measured by iodometric titration, is >97%, whereas the polystyrene section has a hydrogenation degree of <1%.

- Characterization of the polymer.

[0039] The polymer thus obtained is separated into two fractions by means of the dissolution and subsequent precipitation technique. A sample of the polymer is dissolved in tetrahydrofuran (concentration of 0.5% by weight) at 23°C. Over a period of 12 hours the subsequent precipitation of two aliquots of solid (polymer) takes place by the addition of a weight quantity of ethyl alcohol equal to that of the tetrahydrofuran.

[0040] The two polymeric fractions were analyzed by means of gel permeation chromatography using a M.A.L.L.S. (Multi Angle Laser Light Scattering) detector. This technique allows the absolute molecular weight of the polymers to be determined and the branching degree of the various molecular species of which it is formed, to be accurately evaluated. This is made possible by the determination of the average square radius of the polymeric species dissolved in the solvent (the same used as in the gel permeation) obtained by light scattering.

[0041] In the case in question the product is separated into two fractions: the first, corresponding to the product which precipitated after about 10 hours (lower molecular weight), has a weight average Molecular Weight Mw of 80,000, a Mw/Mn ratio of about 1 (typical value in living anionic polymerization) and an α value i.e. of the angular coefficient of the average square radius line against molecular weight [$\langle r \rangle^2 = f(Mw)$], of about 0.6, a typical value of completely linear molecules (see G.P.C., figure 1). The second fraction corresponding to the solid precipitated after 4 hours (fraction with a higher molecular weight) has an Mw of 310,000 and consists of various molecular species (see G.P.C., figure 2) as it has an Mw/Mn of about 2.0. This second fraction also has an average α of 0.393, a value which indicates the presence of several molecular species with different branching degrees.

[0042] · To obtain more accurate information on the molecular weight of the various species contained in fraction Nr. 2 and on their branching degree, and taking into account the mechanism assumed in Journal of Polymer Science, Part A, Polymer Chemistry Vol. 35, pages 17-25, linear molecules are synthesized, having multiple molecular weights with respect to those of the first fraction (80,000). In particular polymers were prepared having a molecular weight of 160,000, 240,000, 320,000, 400,000, 480,000.

[0043] The ratio between the average square radius of the various species present in fraction Nr. 2 and the average square radius of the equivalent linear model molecules (analysis effected by means of M.A.L.L.S.) enabled the presence of various molecular species having branching degrees ranging from 1 to 5 and molecular weights ranging from 160,000 to 480,000, to be identified.

- Formulation of the polymer.

[0044] The polymer thus obtained is used for the preparation of an adhesive formulation with the hot-melt technology.

[0045] The following formulation is prepared:

Polymer of example 1	100 parts by weight;
Escorex 5380 resin	150 parts by weight;
Prisnol Oil	40 parts by weight;
Antioxidants:	
Irganox® 565	0.05 parts by weight;
Irganox® 1010	0.1 parts by weight.

[0046] The adhesive properties of this formulation are indicated in Table 1.

TABLE 1

Properties	
Brookfield Viscosity at 140°C (cps)-ASTM D3236	85,000
Brookfield Viscosity at 160°C (cps)-ASTM D3236	40,000
Brookfield Viscosity at 180°C (cps)-ASTM D3236	8,000
Brookfield Viscosity at 180°C after 4 days (cps)-ASTM D3236	8,000
Polyten tack (g) - ASTM D2979/71	170
Peel adhesion on polyethylene (g/2.5 cm)-PSTC 1	1,600
Holding power (hours) - PSTC 7	75

[0047] The Polyten Tack measurement expresses the adhesive capacity and is expressed in grams.

[0048] The Peel adhesion measurement expresses the adhesive capacity on polyethylene by peeling at 180°C and is expressed in grams.

[0049] The Holding Power measurement expresses the cohesive capacity measured on steel and is expressed in hours.

EXAMPLE 2

[0050] 8400 grams of cyclohexane, 43 ml of tetrahydrofuran and 192 grams of styrene are charged into a 25 litre autoclave. The system is thermostat-regulated at 50°C and 16.5 ml of a 1.5 M solution in n-hexane of sec-butyl-lithium are then added.

[0051] After 30 minutes, 1008 grams of butadiene are added to the polymeric solution thus obtained and the mixture is then left to react for 15 minutes. 10.1 ml of a 1M solution of monobromoethane in cyclohexane are then added, at a temperature of 95°C, and the mixture is left to react for 15 minutes. The polymer thus obtained has a 1,2 chain percentage in the polybutadiene section equal to 45%.

[0052] 4800 grams of the polymeric solution thus obtained are then transferred, in an inert atmosphere (argon), to a 16 litre reactor. 0.310 g of bis cyclopentadienyltitanium di-chloride and 0.904 g of dibutyl-magnesium suitably premixed in cyclohexane are then added to the above solution. The polymeric solution is then brought into an H_2 atmosphere (24 bars) and maintained at a temperature of 100°C, for 60 minutes.

[0053] The polymeric solution is then discharged and the antioxidant (Irganox® 1010, 0.1 phr with respect to the dry product) is added. The solvent is removed by distillation in a vapour stream and the polymer is dried in a fluid bed.

[0054] The polymer thus obtained has a partially branched structure as indicated in formula 1, and an average molecular weight (Mw) of 90,000 and consists of:

(a) a linear fraction (50%) having a molecular weight of 50,000;
(b) a branched fraction (50%) having a molecular weight of 100,000 to 600,000.

[0055] The content of polystyrene with respect to the polymer, measured by means of Fourier transform infrared spectrometry (FTIR), proved to be 20%. The hydrogenation degree of the polybutadiene section, measured by iodometric titration, is >97%, whereas the polystyrene section has a hydrogenation degree of <1%.

[0056] 96 parts of a sample of SINVET® 250 polycarbonate and 4 parts of the copolymer sample of example 2, whose preparation is described above, were fed into an ICMA-MC 33 twin-screw extruder (275°C and 100 rpm of screw revs).

[0057] The mixture was injection moulded at 290°C and 170 bars of pressure. The technological properties were measured on the test-samples thus obtained and are indicated in table 2.

TABLE 2

Properties	Polycarbonate	Polycarbonate + copolymer ex. 2
MFI (g/10 min)	8.5	9.6
Elastic modulus (MPa)	2.380	2.160
Gloss (20°C)	70	65
Izod (23°C) J/m	800	750
Izod (-40°C) J/m	130	660

MFI: ASTM D1238
Elastic modulus: ASTM D 1708
Gloss: ASTM D528-85
Izod: ASTM D256

[0058] From the data of table 2 there is an evident improvement in Izod at -40°C, a characteristic which is lacking in the polycarbonate as such.

EXAMPLE 3

[0059] 8400 grams of cyclohexane, 400 grams of butadiene and 400 grams of styrene are charged into a 25 litre autoclave. The system is thermostat-regulated at 50°C and 18 ml of a 1.5 M solution of sec-butyl-lithium in n-hexane are then added.

[0060] After 30 minutes, 5.7 ml of a 1M solution of tetrahydrofuranpropane and 400 grams of butadiene are added to the polymeric solution thus obtained and the mixture is left to react for 15 minutes. 12.5 ml of a 1M solution of bromoethane in cyclohexane are then added, at a temperature of 95°C, and the mixture is left to react for 15 minutes. The linear fraction of the polymer thus obtained has a $B_1T_1A_2B_2$ structure, wherein B is 15% by weight, T is 30% by weight, A is 22% by weight, B is 33%. The branched fraction has a structure as in general formula (II).

[0061] The polymer thus obtained has a 1,2 chain percentage in the polybutadiene-1 section equal to 15% and 45% in the polybutadiene-2 section. In addition the percentage of alternating butadiene-styrene, i.e. the T segment in general formula (I), is equal to 20% by weight of the monomer.

[0062] 4800 grams of the polymeric solution thus obtained are then transferred to a 16 litre reactor in an inert atmosphere (argon). 0.310 g of bis cyclopentadienyltitanium di-chloride and 0.904 g of dibutyl-magnesium suitably premixed in cyclohexane are then added; the polymeric solution is then brought into an H_2 atmosphere (24 bars) and maintained at a temperature of 100°C for 60 minutes.

[0063] The polymeric solution is then discharged and the antioxidant (Irganox® 1010, 0.1 phr with respect to the dry product) is added. The solvent is removed by distillation in a vapour stream and the polymer is dried in a fluid bed.

[0064] The polymer thus obtained, having the same structure as example 1, has an average molecular weight (Mw) of 109,000 and consists of:

(a) a linear fraction (49%) having a molecular weight of 45,000;
(c) a branched fraction (51%) having a molecular weight of 90,000 to 500,000.

[0065] 80 parts of High Impact polystyrene (HIPS, Edistir® SR 600) and 20 parts of low density polyethylene (LDPE, Riblene® FC 40) are fed into a Bandera-type single-screw extruder, at a temperature of 210°C and 100 rpm. The blend was injection moulded at 210°C and the characteristics are indicated in table 3.

[0066] Using the same extruder and under the same conditions as above, a second composition is prepared using 70 parts of HIPS, 20 parts of LDPE and 10 parts of the copolymer of example 3 prepared as described above. The blend was injection moulded at 210°C and the characteristics are indicated in table 3. The MFI measurement was effected according to ASTM D 1238, the ultimate tensile strength and elongation to break measurements according to ASTM D 638, the flexural modulus measurement according to ASTM D 790 and the Izod measurement according to ASTM D256.

TABLE 3

	HIPS + LDPE	HIPS + LDPE + Copolymer
MFI (g/10 min)	4.7	4.6
Ult. Tens. Strength (MPa)	20	21.4
Elongation to break (%)	40	42
Flexural modulus MPa	1.160	1.130
Izod at 23°C (J/m)	50	120

[0067] The data of table 3 demonstrate the improvement of Izod at 23°C using the copolymer of example 3 of the present invention.

Claims

1. A composition of vinylarene/hydrogenated diene block copolymers, the latter being selected from ethylene-butene and ethylene-propylene, characterized in that it comprises:

    (a) from 30% to 60% by weight of copolymers having linear structures;
    (b) from 70% to 40% by weight of copolymers having branched structures;

    the sum of components (a) and (b) being equal to 100; the weight average molecular weight of the above composition ranging from 30,000 to 400,000.

2. The composition according to claim 1, characterized in that copolymers (a) are from 35 to 50% and copolymers (b) are from 65 to 50%.

3. The composition according to claim 1, characterized in that the weight average molecular weight ranges from 50,000 to 200,000.

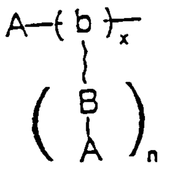
4. The composition according to claim 1, characterized in that the vinylarene content ranges from 2 to 75%.

5. The composition according to claim 4, characterized in that the vinylarene content ranges from 5% to 40%.

6. The polymeric composition according to claim 1, characterized in that the vinylarene is styrene.

7. The polymeric composition according to claim 1, characterized in that:

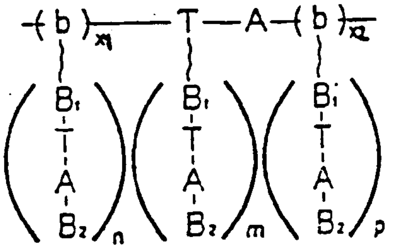
    the linear fraction has structures selected from $(A\text{-}B)_a$ and $(B\text{-}TA\text{-}B)_a$ wherein "a" indicates the number of blocks and is an integer from 1 to 3;
    the branched fraction has structures selected from those having general formula (I)



$$A-\underset{\left(\underset{A}{\overset{|}{\underset{|}{B}}}\right)_n}{\left(\underset{|}{b}\right)_x}- \qquad (I)$$

wherein:

1) A is the polyvinylarene block;
2) b is the monomeric unit of hydrogenated diene, selected from ethylene-butene and ethylene-propylene;
3) x is the number of monomeric units which form the ethylene-butene or ethylene-propylene block;
4) B is the hydrogenated polydiene block $-(b)_x-$;
5) n is the number of branches of the copolymer and is an integer ranging from 1 to 5;
6) B-A is the block copolymer grafted onto the hydrogenated polydiene fraction $-(-b-)_x-$;
or from those having general formula (II):



(II)

wherein:
7) A, B and b have the meaning defined above;
8) x_1 and x_2 are the number of hydrogenated diene monomeric units which form the two ethylene/butene or ethylene/propylene blocks;
9) T is the statistic terpolymer consisting of vinylarene/ethylene-butene or vinylarene/ethylene-propylene, the content of T being from 0 to 30% by weight of the compound having general formula (II);
10) $-B_1-T-A-B_2$ is the block copolymer grafted onto $-(-b-)_{x1}-T-A-(-b-)_{x2}-$;
11) (m+n+p) is the number of branches of the copolymer $-B_1-T-A-B_2$ grafted and ranges from 1 to 5.

8. A process for the preparation of the polymeric composition according to claim 1, which comprises the following steps:

a) reaction of a vinylarene, as such or mixed with a conjugated diene, with an organo-derivative of Lithium having the general formula R-Li wherein R is a monofunctional hydrocarbon radical selected from aliphatic and cycloaliphatic radicals with from 2 to 20 carbon atoms;
b) reaction of the mixture coming from step (a) with a conjugated diene;
c) reaction of the mixture coming from step (b) with a bromo-derivative having the general formula R'-Br in an essentially stoichiometric quantity with respect to the Lithium, wherein R' is a C_1-C_{10} monofunctional hydrocarbon radical selected from alkyl, cycloalkyl and aryl radicals; thus obtaining a composition of non-hydrogenated block copolymers;
d) hydrogenation of the polydiene section of the composition of non-hydrogenated block copolymers obtained in step (c) to give the composition of hydrogenated block copolymers according to claim 1.

9. The process according to claim 8, characterized in that the vinylarene is styrene and the conjugated diene is selected from isoprene and butadiene, and is preferably butadiene.

10. The process according to claim 8, characterized in that R' is a C_1-C_3 alkyl radical, and is even more preferably ethyl.

11. A formulation of adhesives and seals characterized in that it comprises the polymeric composition according to claim 1.

12. A polymeric composition comprising engineering polymers, selected from polyesters, polyamides and polycarbonates, preferably polycarbonate, and the mixture of block copolymers according to claim 1.

13. A polymeric composition comprising polyethylene, polystyrene and the mixture of block copolymers according to claim 1.

Fig.1

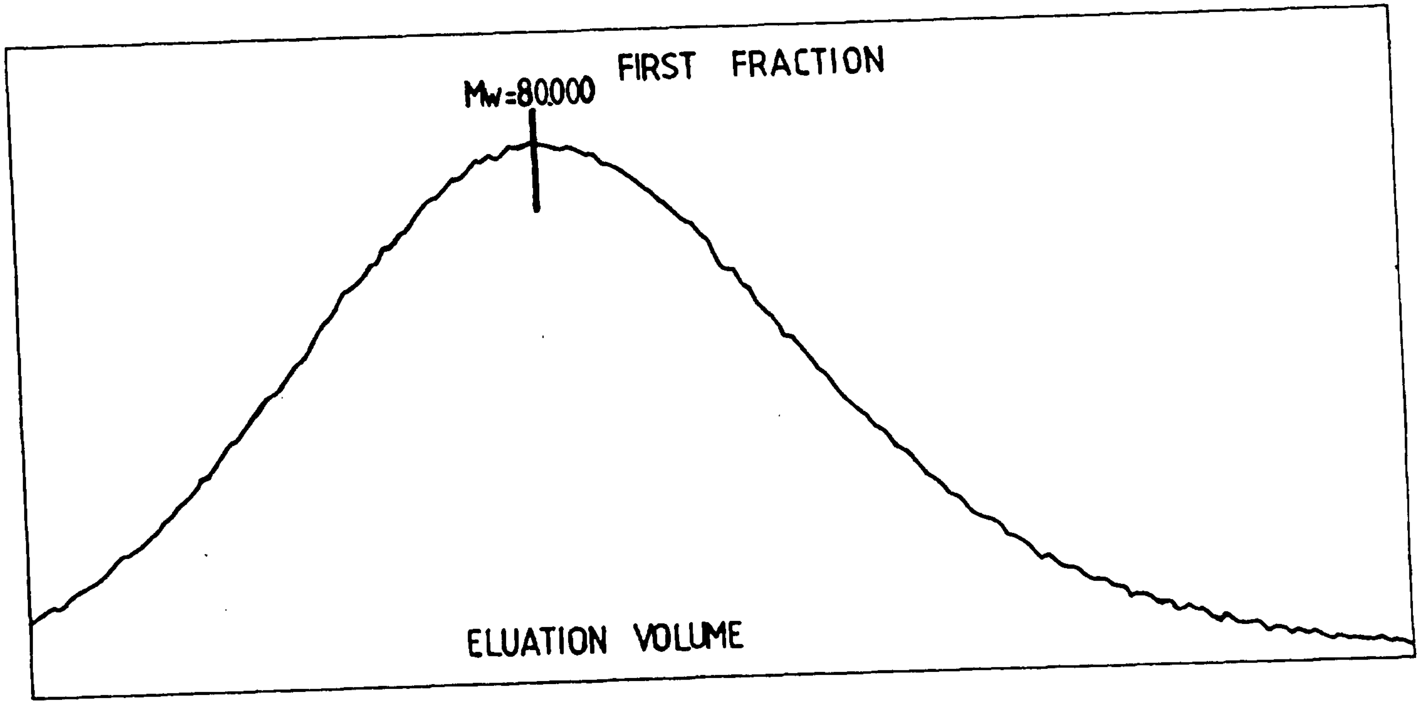
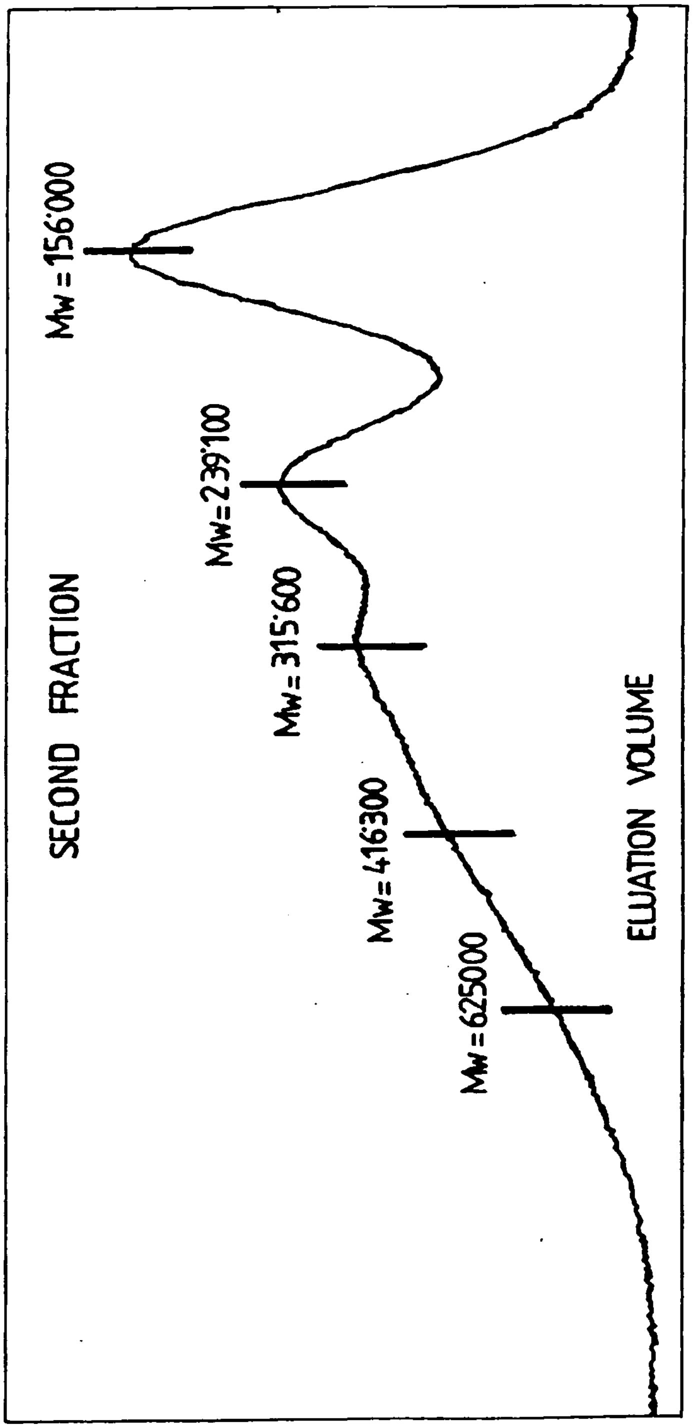


Fig.2


SECOND FRACTION
Mw = 156'000
Mw=239'100
Mw= 315'600
Mw= 416'300
Mw=625000
ELUATION VOLUME

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2818

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X Y	EP 0 757 066 A (ENICHEM ELASTOMERS) 5 February 1997 (1997-02-05) * claims 1-3,5 * * page 2, line 26-40 * ---	1-6,8,9,11 12,13	C08L53/02 C08F297/04
Y	EP 0 215 501 A (SHELL INT RESEARCH) 25 March 1987 (1987-03-25) * abstract * ---	12	
Y	EP 0 471 998 A (ENICHEM ELASTOMERS) 26 February 1992 (1992-02-26) * claim 11 * ---	13	
Y	EP 0 683 187 A (ENICHEM ELASTOMERS) 22 November 1995 (1995-11-22) * claims 1-10 * * abstract * ---	1-6,8-11	
D,Y	GB 2 225 330 A (ENICHEM ELASTOMERS) 30 May 1990 (1990-05-30) * abstract ; page 7, line 11-20 * * page 3, line 12-18 * ---	1-6,8-11	
A	EP 0 404 185 A (NIPPON ZEON CO) 27 December 1990 (1990-12-27) * claims 1-6 * * abstract * ---	1-13	
A	EP 0 704 477 A (BASF AG) 3 April 1996 (1996-04-03) * abstract * -----	1-13	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C08L
C08F
C09J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 November 1999	Hammond, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 20 2818

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-11-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0757066 A	05-02-1997	IT MI951727 A	04-02-1997
		JP 9291266 A	11-11-1997
EP 0215501 A	25-03-1987	US 4783503 A	08-11-1988
		US 4797447 A	10-01-1989
		AT 67770 T	15-10-1991
		AU 595536 B	05-04-1990
		AU 6115386 A	19-02-1987
		BR 8603882 A	24-03-1987
		CA 1277056 A	27-11-1990
		CN 1012066 B	20-03-1991
		CN 1050881 A,B	24-04-1991
		DE 3681670 A	31-10-1991
		DK 388286 A	17-02-1987
		ES 2000871 A	16-03-1988
		KR 9404123 B	13-05-1994
		US H724 H	02-01-1990
		US H731 H	06-02-1990
		US 4988765 A	29-01-1991
		US 4954568 A	04-09-1990
		JP 62041213 A	23-02-1987
		US 4868245 A	19-09-1989
		US H790 H	05-06-1990
		US 4898914 A	06-02-1990
		US H1438 H	02-05-1995
		CA 1260173 A	26-09-1989
EP 0471998 A	26-02-1992	IT 1246410 B	18-11-1994
		AT 149188 T	15-03-1997
		CA 2047612 A	26-01-1992
		DE 69124756 D	03-04-1997
		DE 69124756 T	24-07-1997
		ES 2097772 T	16-04-1997
		FI 913552 A	26-01-1992
		JP 5132533 A	28-05-1993
		MX 9100347 A	28-02-1992
		US 5395894 A	07-03-1995
		US 5314951 A	24-05-1994
EP 0683187 A	22-11-1995	IT 1269803 B	15-04-1997
		AT 166898 T	15-06-1998
		CN 1117070 A	21-02-1996
		DE 69502771 D	09-07-1998
		DE 69502771 T	24-09-1998
		ES 2118467 T	16-09-1998
		JP 8060124 A	05-03-1996

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 99 20 2818

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-11-1999

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0683187	A		SI	683187	T	31-08-1998
			US	5627234	A	06-05-1997
GB 2225330	A	30-05-1990	IT	1227927	B	14-05-1991
			BE	1003077	A	12-11-1991
			CA	2003057	A	25-05-1990
			CN	1044107	A,B	25-07-1990
			DE	3938927	A	31-05-1990
			DK	592089	A	26-05-1990
			ES	2029153	A	16-07-1992
			FR	2639641	A	01-06-1990
			MX	169894	B	29-07-1993
			NL	8902892	A	18-06-1990
			SE	501518	C	06-03-1995
			SE	8903825	A	26-05-1990
			US	5164455	A	17-11-1992
EP 0404185	A	27-12-1990	JP	2071223	C	10-07-1996
			JP	3026747	A	05-02-1991
			JP	7098890	B	25-10-1995
			CA	2019596	A	23-12-1990
			DE	69007344	D	21-04-1994
			DE	69007344	T	11-08-1994
			US	5075377	A	24-12-1991
EP 0704477	A	03-04-1996	DE	4434602	A	04-04-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82